

# Towards accurate *ab initio* predictions of the spectrum of methane

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(Draft version July 20, 2001)

## Abstract

We have carried out extensive *ab initio* calculations of the electronic structure of methane, and these results are used to compute vibrational energy levels. We include basis set extrapolations, core-valence correlation, relativistic effects, and Born-Oppenheimer breakdown terms in our calculations. Our *ab initio* predictions of the lowest lying levels are superb.

## I. INTRODUCTION

Methane is an important molecule in many fields, including astrophysics<sup>1</sup> and the study of greenhouse gases.<sup>2</sup> Knowledge of the spectrum from experiment is hampered with the difficulties in analyzing the complex spectrum. Thus it is our goal to provide accurate theoretical data for this system.

In the past, the technique for achieving this was empirical fits to experimental results using model hamiltonians.<sup>3</sup> This, however, has limited predictive capabilities, thus it is desirable to advance the state of the art to enable reliable *ab initio* predictions of the spectrum.

In this paper we report *ab initio* calculations of vibrational levels of methane. *Ab initio* is a rather vague term. It encompasses a potential energy surface (PES) based on the SCF method to sophisticated CI and coupled cluster methods, and ro-vibrational calculations using the normal-mode, rigid rotator approach based on a second order PES to variational methods with exact kinetic energy operators and involved representations of the PES. These methods can give energy levels that in worst cases have errors of hundreds of  $100\text{ cm}^{-1}$ , and in best cases have errors of about  $5\text{ cm}^{-1}$ , or so. This level of accuracy is not sufficient.

In a previous publication,<sup>4</sup> we reported sophisticated *ab initio* calculations of methane of the type mentioned above. In the present work, in contrast, we are attempting to make the errors from our approximations as small as possible. Our PES is an eighth order expansion and includes extrapolations of the 1-particle basis, corrections of the correlation treatment to the full CI limit, core-valence correlation, scalar relativity, the lamb shift, and the first order correction to the Born-Oppenheimer approximation. In our nuclear motion calculations, we use a variational method using an exact kinetic energy operator plus an approximate inclusion of *ab initio* second order corrections to the Born-Oppenheimer approximation (non-adiabatic corrections). We believe this is the first molecule containing more than two electrons where such complete *ab initio* calculations have been carried out. We will see that this yields results that are in excellent agreement with experimental data for low lying levels.

## II. ELECTRONIC STRUCTURE CALCULATIONS

The PES of the present work is an extension of our previous PES for methane.<sup>4</sup> We use the same functional form, an eighth order expansion in symmetry coordinates based on Radau coordinates and a local mode correction function, and we determined the coefficients by least squares fitting. In our previous work, we fit 7579 points out of a list of 7924 points.<sup>4</sup> For the present work, we have computed 7923 of the 7924 points: one point had two hydrogen atoms too close together for the electronic structure calculations, and this point is discarded in all fits. Subsequently we discovered an error in generating the points. When we corrected the error, a total of 8268 points were generated. Thus in the present work, some of the seventh and eighth order coefficients are not as well determined as they could be. In future work we will correct this problem. The same local mode correction function was used as in our previous PES. All electronic structure calculations were carried out with a modified version of Molpro 2000.1<sup>7</sup> using the correlation consistent 1-particle basis sets of Dunning<sup>8</sup> denoted cc-pVXZ with X=T,Q, or 5. Unless explicitly stated otherwise, all our correlated calculations restricted the carbon like 1s orbital to be doubly occupied in all configurations.

Our previous PES was based on the CCSD(T) energies determined with the cc-pVTZ basis set.<sup>4</sup> To estimate the deviations from full CI, we have also carried out calculations using icACPF method with the full valence CASSCF reference space. The CCSD(T) method recovers more correlation energy than the icACPF method for methane in the vicinity of the minimum with this basis set, but the icACPF method will dissociate properly and give a more systematically correct PES at all geometries. We have compared the CCSD(T) and icACPF results and find no indication that the CCSD(T) method is breaking down, so we judge both methods as roughly equally reliable in the present situation.

There are several ways one can estimate the full CI PES using these results. First of all, one can just compare the results from the CCSD(T) and icACPF calculations, however neither method recovers all the correlation energy. Császár<sup>5</sup> has recently shown that the

approximation

$$E^{FCIb} = E^{SCFb} + c^b \Delta E^{CCSD(T)b}, \quad (1)$$

where  $E^{FCIb}$  is the full CI energy in basis  $b$ ,  $E^{SCFb}$  is the SCF energy in basis  $b$ , and  $E^{SCFb} + \Delta E^{CCSD(T)b}$  is the CCSD(T) energy in basis  $b$ , worked rather well for a series of test molecules, and furthermore the scale factor  $c^b$  was only weakly dependent on 1-particle basis set. Thus the scale factor can be determined from *ab initio* calculations in a small basis set where one can afford to do a full CI calculation. This result was anticipated somewhat by the work of Brown and Truhlar<sup>6</sup> who attempted to produce results accounting for incompleteness of the 1-particle basis and incompleteness in the CI treatment by writing

$$E^{FCIc} = E^{CASSCFb} + s^b \Delta E^{MRCIb}, \quad (2)$$

where  $E^{FCIc}$  is the full CI result in basis  $c$ ,  $E^{CASSCFb}$  is the CASSCF energy in basis  $b$ , and  $E^{CASSCFb} + \Delta E^{MRCIb}$  is the MRCI energy. Normally  $c$  was taken to be a complete basis in which case  $s^b$  was determined using some experimental data, however early test calculations were carried out with  $c = b$ . These calculations indicated the scale factor had very weak geometry dependence. Thus we will use

$$E^{FCIb} = E^{CASSCFb} + s^b \Delta E^{icACPFb} \quad (3)$$

as our second prediction of the full CI energy.

We can determine the parameters  $c^b$  and  $s^b$  using two *ab initio* methods. In the first we perform a full CI calculations in a small basis, specifically cc-pVDZ on C and cc-pVDZ minus  $p$  functions on the H atoms. We currently can not afford a full CI calculation using the full cc-pVDZ basis on the H atoms. We carried out calculations near the minimum geometry, and did not correlate the C 1s like orbital, which was constrained to be the SCF orbital in all calculations. This yielded the scale factors 1.00318 for CCSD(T) and 1.00359 for icACPF. In these calculations, the icACPF energy is less than the CCSD(T) energy. However in the cc-pVTZ basis, the CCSD(T) energy was less than the icACPF energy, thus

these scale parameters are clearly not basis independent. This motivates our second *ab initio* method. Here we choose the scale factors so that the scaled CCSD(T) results equal the scaled icACPF results. Specifically, we used the equation

$$0 = E^{SCFb} + c^b \Delta E^{CCSD(T)b} - E^{CASSCFb} - s^b \Delta E^{icACPFb} + t^b \Delta E^{core} \quad (4)$$

to determine the parameters, where  $\Delta E^{core}$  is core-valence correlation correction defined below. This term is included because the CCSD(T) calculations use the SCF 1s orbital whereas the icACPF calculations use the CASSCF 1s orbital. We determine the parameters by a least square fit to the data at the 7923 points. This yields  $c_b = 1.0075972$ ,  $s_b = 1.0371217$ , and  $t_b = 0.054869$ . We see that the icACPF scaling factor changed a great deal more than the CCSD(T) factor. So from this data we can determine three estimates of the full CI energy, namely  $E^{SCFb} + c^b \Delta E^{CCSD(T)b}$ , which we call  $V^{CCSD(T)x}$ ,  $E^{CASSCFb} + s^b \Delta E^{icACPFb} - t^b \Delta E^{core}$ , which we call  $V^{icACPFx}$ , and the average of the two. We call the average of the two  $V^a$ . It is uncertain how reliable this procedure is. One measure is the degree to which all three estimates agree.

We next turn to the question of 1-particle basis. There have been many ways proposed to extrapolate to the limit of complete 1-particle basis, starting with the exponential fitting of the correlation consistent basis sets by Woon and Dunning.<sup>9</sup> Halkier *et al.*<sup>10,11</sup> studied the convergence of the correlation and SCF energies, and found that an exponential form was more suitable for the SCF energy and that an inverse power form was more suitable for the correlation energy. For the correlation energy, they find that their best results are obtained using two point extrapolation using the results of the largest basis sets possible.<sup>10</sup> For the SCF energy, they find that extrapolation is not always reliable, but the most reliable form is the exponential form using the largest two basis sets possible with the nonlinear parameter  $\alpha$  fixed at 1.63. In the present work, we will extrapolate the results of CCSD(T) calculations using the cc-pVTZ and cc-pVQZ basis at all 7923 points using formulas involving three parameters, but determine one of the parameters from limited results using the cc-pV5Z basis. Since we are using limited data from a larger basis set in our extrapolation, we have

a different case than what Halkier *et al.* considered. Our three parameter form for the correlation energy is inspired by the work of Varandas<sup>12</sup>. In detail the form we used was

$$E_X = E_\infty + B \exp(-\alpha X), \quad (5)$$

to extrapolate the SCF energy, and

$$E_X^{cor} = E_\infty^{cor} + A_3 Y, \quad (6)$$

with

$$Y = X^{-3}(1 + A_4 X^{-1}), \quad (7)$$

for the correlation energy, where  $X = 3$  for cc-pVTZ basis,  $X = 4$  for cc-pVQZ basis, etc. This differs from Varandas in that he divides the  $A_3$  term by  $E_\infty^{cor}$  and takes  $A_4$  to be a function of  $A_3$ . We find it more expedient to use the above form with  $A_4$  a constant, and furthermore we split the correlation energy into the MP2 part and the difference between the CCSD(T) energy and the MP2 energy, and extrapolate the two parts separately. To determine  $\alpha$  for the SCF energy and  $A_4$  for the MP2 energy and CCSD(T)–MP2 energy, we carried out calculations using the cc-pV5Z basis set. These calculations are very expensive, and we have results for the SCF and CCSD methods the 203 of the 205 points our algorithm generates for the quartic expansion of the PES, and CCSD(T) results at 115 of the geometries. For the SCF energy, at all the geometries for which we have cc-pV5Z energies, we fit them to the above formula, and determine the average of the parameter  $\alpha$ . We obtain  $\alpha = 1.3342(9 \times 10^{-4})$ , where the number in parenthesis is the root-mean-square deviation (rms) from the average. Using this average value and the cc-pVTZ and cc-pVQZ SCF energies to predict the cc-pV5Z results, we obtain a rms error of  $0.14 \text{ cm}^{-1}$ . For the MP2 energy, we find  $A_4 = -0.178(6 \times 10^{-3})$ , and we predict the cc-pV5Z basis MP2 results with an rms error of  $0.6 \text{ cm}^{-1}$ . Finally for the difference between the CCSD(T) and MP2 energies, we find  $A_4 = -2.092(3 \times 10^{-3})$ , and we predict the cc-pV5Z results with an rms error of  $1.1 \text{ cm}^{-1}$ . The difference between this extrapolated and scaled energy and the cc-pVTZ scaled energy is added to  $V^a$  to yield  $V^{ab}$ .

Next we include the core-valence correction. To do this we used a special 1-particle basis.<sup>13</sup> This is derived from the aug-cc-pVTZ basis. The aug-cc-pVTZ basis on C takes the form  $(11s\ 6p\ 3d\ 2f)/[5s\ 4p\ 3d\ 2f]$ . The six inner  $1s$  primitive functions are contracted to two functions using the coefficients from the cc-pVTZ basis set, and the 5 outer  $1s$  functions are included uncontracted. The  $p$  functions are uncontracted. The  $d$  functions are augmented by two tighter functions with the exponential parameters 3.29 and 9.87. These are obtained as an even tempered expansion of the  $d$  space using the ratio 3.0. The diffuse  $f$  function is deleted and one tighter function added with exponential parameter 3.92, which is chosen to be 1.2 times the first tight  $d$  exponential parameter. On the H atoms, the aug-cc-pVTZ basis is used uncontracted, except the diffuse  $d$  function is deleted. This basis set is used with the CCSD(T) method in a calculation correlating all electrons and a calculation correlating only the valence electrons. These calculations are carried out at all 7923 geometries, and the difference is called  $\Delta E^{core}$ . This is scaled by  $c_b$  and added to  $V^{ab}$  to yield  $V^{abc}$ .

To include scalar relativity, we used the Douglas-Kroll-Hess method.<sup>15-17</sup> The 1-particle basis was the cc-pVTZ basis recontracted for the atoms including the relativistic correction. Then calculations were carried out at the 7923 geometries using the CCSD(T) method. The difference between the CCSD(T) energies using the cc-pVTZ basis and these calculations is added to  $V^{abc}$  to yield  $V^{abcr}$ . In these calculations, the Douglas-Kroll integrals were generated using the MOLCAS code,<sup>18</sup> and the integrals read into and used by the MOLPRO code.

The radiative correction, or Lamb shift, is included following the procedure of Pyykkö *et al.*,<sup>14</sup> with the Darwin term it depends on computed during the icACPF calculation. This is added to  $V^{abcr}$  to yield  $V^{abcrr}$ .

The first order correction to the Born-Oppenheimer approximation was computed using the Handy method<sup>19</sup> with the cc-pVTZ basis for the full valence CASSCF wavefunction.<sup>20</sup> Because of its expense, this was only calculated at the 1746 geometries our algorithm produces to determine an sextic expansion. This correction was fit using an sextic expansion in symmetry coordinates without the local mode correction function. The coefficients of this fit were added to the coefficients of the fit to  $V^{abcrr}$  to yield the PES  $V^{abcrr1}$ . This is our

most accurate *ab initio* PES. It is difficult to judge the accuracy of this correction. Our calculations on the  $H_2$  molecule,<sup>20</sup> showed that a valence CASSCF yields results only of qualitative accuracy, but at the moment, this is the best calculations we can perform. The limitation to sixth order is probably not too severe, since the points are fit very well.

The second order correction to the Born-Oppenheimer approximation followed the procedures described in Ref. 20. We use the aug-cc-pVTZ basis set and the SCF approximation for the ground state and the CI-singles approximation for the excited states. We made a single calculation at the CCSD(T) cc-pVTZ minimum energy geometry. One measure of the reliability of these calculations is to consider the rotational  $g$  factor, which is determined from similar formulas.<sup>20</sup> For methane, we compute 0.3824, while the experimental result is 0.3133.<sup>21</sup> Thus we recover about 90% of the electronic contribution to the rotational  $g$  factor, which is very typical in our experience. To evaluate the non-adiabatic correction, it is necessary to know the differential form of the nuclear kinetic energy operator. Our rovibrational code is based on the five atom Radau coordinates.<sup>25</sup> The four Radau vectors are grouped into two pairs, and the kinetic energy operator for each pair is that of a triatomic. See *e.g.* Sutcliffe and Tennyson.<sup>22</sup> To aid in the use of symmetry, we hypersphericalize the four radial coordinates to form the grand hyperradius,  $\rho_{1234}$ , which is totally symmetric, and three hyperangles  $\chi_{1234}$ ,  $\chi_{13}$ , and  $\chi_{24}$ , which span the triply degenerate stretch. For the rotation-bending degrees of freedom, we use bisect embedding ( $a=1/2^{22}$ ) and choose the body-fixed axes so that the  $z$  axis bisects the first pair of Radau vectors and that they lie in the  $xz$  plane. The internal coordinates are  $\chi_i$ , the angle between the  $i$ 'th pair of vectors, and  $\tilde{\alpha}\tilde{\beta}\tilde{\gamma}$ , the Euler angle rotating the axes of the second pair to the first. Thus the kinetic energy operator takes the form

$$T^{nuc} = T^{vib} + T^{rb1} + T^{rb2}, \quad (8)$$

with

$$T^{vib} = T_{\rho_{1234}} + T_{\chi_{1234}} + T_{\chi_{13}} + T_{\chi_{24}}, \quad (9)$$

and



$$T^{rb1} = T_{x1} + N^{(1)}(\tilde{J}_y + L_y) + \sum_{\alpha\beta} M_{\alpha\beta}^{(1)}(\tilde{J}_\alpha + L_\alpha)(\tilde{J}_\beta + L_\beta), \quad (10)$$

$$T^{rb2} = T_{x2} + N^{(2)}\tilde{L}_y + \sum_{\alpha\beta} M_{\alpha\beta}^{(2)}\tilde{L}_\alpha\tilde{L}_\beta, \quad (11)$$

where  $N^{(i)}$  and  $M^{(i)}$  are inverse moment of inertia like quantities<sup>22</sup> for vector pair  $i$ ,  $J_\alpha$  is the total nuclear angular momentum operator with respect to body-fixed axis  $\alpha$ , and  $L_\alpha$  is the second vector pair total angular momentum operator with respect the the body-fixed axis  $\alpha$ . In the above equation, tilde indicates that the body-fixed rather than space-fixed formulas for the angular momentum operators are to be used,<sup>26</sup> except the body-fixed components are reversed to give rise to normal commutation relations. We will make the approximation that the correction functions are independent of geometry, and furthermore neglect all terms involving derivatives not already present in the kinetic energy operator. We found that this is quite accurate for H<sub>2</sub>O.<sup>20</sup> Thus the non-adiabatic correction consists of adding to the kinetic energy operator the quantity

$$c_{ss}T_{\rho_{1234}} + c_{ds}(T_{\chi_{1234}} + T_{\chi_{13}} + T_{\chi_{24}}) + c_b(T_{x1} + T_{x2}) + \sum_{\alpha} c_{\alpha\alpha} \left( M_{\alpha\alpha}^{(1)}[\tilde{J}_\alpha + L_\alpha]^2 + M_{\alpha\alpha}^{(2)}\tilde{L}_\alpha^2 \right), \quad (12)$$

where  $c_{ss} = -2.83 \times 10^{-4}$ ,  $c_{ds} = -4.85 \times 10^{-4}$ ,  $c_b = -1.60 \times 10^{-4}$ ,  $c_{xx} = -1.82 \times 10^{-4}$ ,  $c_{yy} = -2.85 \times 10^{-4}$ , and  $c_{zz} = -2.63 \times 10^{-4}$ . In comparison, the difference between using the nuclear masses and atomic masses is  $-5.4 \times 10^{-4}$ .

### III. VIBRATIONAL CALCULATIONS

Our vibrational calculations were carried out using the same program as our previous work,<sup>4</sup> except it has been modified to incorporate the non-adiabatic corrections. A full description of the algorithm will be given elsewhere.<sup>25</sup> In brief, highly optimized stretching and bending basis functions are determined self consistently and full symmetry is used in the final diagonalization. The only approximations are those inherent to a finite basis expansion. The critical parameters determining the accuracy of our calculations are  $E_{master} = 0.2 E_h$ ,

$IDR12 = 32$ ,  $IDR3 = 32$ ,  $KMDIF = 10$ ,  $ICUPCHI = 22$ , and  $E_{cutccabg} = 0.03586 E_h$ . The quantity  $E_{master}$  is the default energy criterion, and this controls the generation of basis functions and the size of the final matrix to be diagonalized.<sup>24,23</sup>  $IDR12$  is the number of primitive basis functions used for  $\chi_1$  and  $\chi_2$ , and  $ICUPCHI$  is the number of contracted  $\chi_i$  function used to form coupled  $\chi_1\chi_2$  basis functions. The variable  $IDR3$  specifies the maximum  $\ell$  quantum number used in the primitive basis for coordinates  $\tilde{\alpha}\tilde{\beta}\tilde{\gamma}$ , and  $KMDIF$  is the maximum absolute difference between the two  $m$  indices on the primitive basis for coordinates  $\tilde{\alpha}\tilde{\beta}\tilde{\gamma}$ .  $E_{cutccabg}$  is the maximum energy above the zero point energy of contracted  $\tilde{\alpha}\tilde{\beta}\tilde{\gamma}$  functions to use in the calculations.

We carried out calculations for the  $V^{CCSD(T)}$  PES, without including non-adiabatic effects, and used the optimized basis functions for this PES for all other PES that we considered. It takes about 24 hours for the initial PES and symmetry block and about 2 hours for each subsequent calculation on a SGI Origin 2000 (250 MHZ IP27 processors). We converted to  $\text{cm}^{-1}$  from hartree atomic units using the factor 219474.63148245297, and we used the nuclear masses 1836.15264064782696 for H atoms and 21868.66175734604620 for carbon.

#### IV. RESULTS AND DISCUSSION

In Fig.(1-4) we plot calc-exp as a function of vibrational energy for selected PES. In table 1 we give all of our results. Figure 1 shows the results using the CCSD(T) method and cc-pVTZ basis. The results are scattered about zero with a rms deviation of  $6.5 \text{ cm}^{-1}$ . A couple of levels accidentally happen to agree with experiment very well. In fig. (2) we show the results of using the PES  $V^{ab}$ . The potentials falling intermediate in sophistication between CCSD(T) and  $V^{ab}$  give results very similar to fig.(1). In comparison to fig. (1), the grouping of the errors is much tighter about the zero line, except for a few apparent outliers. As before, there are a couple of levels accidentally agreeing very well with experiment, but they are different levels than in fig. (1). In fig. (3) we show the results of  $V^{abc}$ , and the main result compared to fig.(2) is a shifting upwards of the errors, with only one level agreeing

very well with experiment. The effect of relativity and the Lamb shift are very small in methane, so the next PES we consider is  $V^{abcorr1}$  with the non-adiabatic corrections, and the results for this calculation are shown in fig.(4). In comparison to the previous figures we see for the first time that the lowest energy levels are uniformly in excellent agreement with experiment. The lowest seven levels all have errors less than  $0.7 \text{ cm}^{-1}$ . This is a very encouraging result.

What about the higher levels, which have errors up to  $23.4 \text{ cm}^{-1}$  in our best calculations? There are several possible sources of error, including experimental error. However more likely is our fit to the *ab initio* data. In our least square fits to the 7923 points, we use variable weights, with the weights beginning to become very small at about  $13,000 \text{ cm}^{-1}$  above the minimum. This cut off was chosen because the density of points rapidly decreases above this energy, and the very high energy points are much harder to fit accurately. However the first level having error greater than  $1 \text{ cm}^{-1}$  in our best calculation has a total energy of about  $12,600 \text{ cm}^{-1}$  above the minimum. The proximity to  $13,000 \text{ cm}^{-1}$  is likely no co-incidence.

This raises an interest issue. In our previous work on methane,<sup>4</sup> we argued that it was appropriate to consider energy along a single mode to decide how high it was necessary for a PES to be accurate. This is certainly true if the PES is separable. This was also motivated by how high the zero point energy is for methane. At  $9700 \text{ cm}^{-1}$ , it is an appreciable fraction of a CH bond energy. Extrapolating to larger molecules, the zero point energy of pentane is probable larger than a CH bond energy. It just does not seem reasonable to have to know the PES up to dissociation just to obtain the zero point energy! However the present results seem to indicate that if one is interested very accurate results, very large portions of the PES need to be known, and known well.

In future work we plan to increase our grid to cover the full 8268 points and fit the higher energy points more accurately.

Two other possibilities will likely also play a role. First is the extrapolation to full CI and the second is the first order correction to the Born-Oppenheimer approximation. To see this, we note that the lowest levels with errors greater than  $1 \text{ cm}^{-1}$  are the stretching

fundamentals. These are also the first levels for which the calculations using the unextrapolated CCSD(T) and icACPF potentials significantly differ. Since CCSD(T) does not dissociate properly, while icACPF does, our full CI extrapolation procedure may be weighting CCSD(T) too highly. Using a PES closer to icACPF looks like it would improve the agreement for these stretching levels. How to improve on this using *ab initio* techniques is not clear.

The reason we think that the first order correction to the Born-Oppenheimer approximation is also implicated is based on our previous results for  $H_2$  and  $H_2O$ . For  $H_2$ , we observed a big difference between SCF and valence CASSCF based corrections, with the CASSCF results being only qualitatively correct. For  $H_2O$ , we did not have accurate results to compare to, but the SCF and CASSCF results for the stretching modes differed, in agreement with the stretching motion in  $H_2$ . In contrast, the SCF and CASSCF results for the bend were in excellent agreement for  $H_2O$ . Presumably this means that the correction for the bend is well described, while the stretches are less well described. Since the levels that are well described in methane are also bends, the same effect is probably occurring. We hope to develop methods to compute the first order correction more accurately which should enable us to minimize the errors it produces.

## V. CONCLUSIONS

We have computed vibrational levels for methane from a series of PES of increasing sophistication. Only the results obtained from our best PES and including non-adiabatic corrections gives uniform good agreement ( $< 1 \text{ cm}^{-1}$  error) with experiment for low lying levels. Given the current level of agreement with experiment, the relativistic and Lamb shift corrections to the PES are negligible, although they will be important if the remaining corrections become more accurate.

It appears that good agreement with experiment for the higher levels requires a PES that is more accurate higher than  $13,000 \text{ cm}^{-1}$  above the minimum, more accurate treatment of

electron correlation, or a more accurate first order correction to the Born-Oppenheimer approximation.

## VI. ACKNOWLEDGEMENTS

We would like to thank Harry Partridge for the core basis set and discussions about this project, and Duane Carbon for assistance in obtaining computer time. This project was funded by the NASA Office of Space Studies, Planetary Atmospheres Program.

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# TABLES

TABLE I. Vibrational Energy Levels in  $\text{cm}^{-1}$ .

label	CC <sup>a</sup>	CI <sup>b</sup>	CCx <sup>c</sup>	CIx <sup>d</sup>	V <sup>a</sup>	V <sup>ab</sup>	V <sup>abc</sup>	V <sup>abcr</sup>	V <sup>abcr</sup>	V <sup>abcr</sup>	V <sup>abcr</sup>	non-ad <sup>e</sup>	exp. <sup>f</sup>	band
1A1	9691.53	9681.24	9687.80	9686.75	9687.27	9695.19	9710.08	9710.11	9710.10	9713.04	9711.36			z.p.e
1F2	1311.77	1312.14	1310.89	1311.21	1311.05	1310.27	1312.17	1312.34	1312.33	1311.04	1310.94	1310.76	0001	
1E	1533.27	1532.65	1532.49	1532.02	1532.25	1531.44	1533.51	1533.82	1533.80	1533.85	1533.73	1533.33	0101	
2A1	2589.95	2590.51	2588.23	2588.78	2588.51	2585.68	2589.56	2589.87	2589.85	2587.34	2587.10	2587.04	0002	
2F2	2616.37	2617.00	2614.61	2615.19	2614.90	2613.27	2617.15	2617.48	2617.45	2614.93	2614.67	2614.26	0002	
2E	2627.45	2628.15	2625.70	2626.34	2626.02	2623.32	2627.14	2627.49	2627.46	2624.92	2624.70	2624.62	0002	
3F2	2831.77	2831.34	2830.16	2829.94	2830.05	2827.99	2832.00	2832.45	2832.42	2831.24	2831.01	2830.32	0101	
1F1	2847.06	2846.81	2845.40	2845.25	2845.32	2843.80	2847.79	2848.27	2848.24	2847.01	2846.71	2846.08	0101	
3A1	2913.72	2909.86	2912.65	2913.33	2912.99	2914.50	2920.48	2920.43	2920.44	2919.25	2918.87	2916.48	1001	
4F2	3013.83	3008.24	3012.90	3011.92	3012.41	3017.46	3023.94	3023.80	3023.81	3024.07	3023.38	3019.49	0011	
4A1	3063.77	3062.40	3062.20	3061.30	3061.75	3060.37	3064.57	3065.17	3065.14	3065.29	3064.98	3063.65	0201	
3E	3065.29	3064.03	3063.72	3062.80	3063.26	3061.69	3065.83	3066.45	3066.41	3066.53	3066.22	3065.14	0201	
5F2	3878.40	3879.14	3875.83	3876.60	3876.22	3871.77	3877.70	3878.14	3878.11	3874.42	3874.09	3870.49	0003	
5A1	3917.75	3918.52	3915.13	3915.91	3915.52	3913.04	3918.98	3919.44	3919.41	3915.73	3915.36	3909.18	0003	
2F1	3930.05	3930.90	3927.43	3928.27	3927.85	3924.36	3930.27	3930.76	3930.72	3927.03	3926.66	3920.50	0003	
6F2	3940.98	3941.92	3938.37	3939.28	3938.83	3934.19	3940.04	3940.55	3940.51	3936.79	3936.46	3930.92	0003	
4E	4109.07	4108.74	4106.63	4106.62	4106.63	4102.54	4108.56	4109.13	4109.10	4106.75	4106.39	4105.15	0102	
3F1	4136.57	4136.32	4134.08	4134.10	4134.09	4130.89	4136.93	4137.52	4137.48	4135.11	4134.63	4128.57	0102	



6A1 4140.26 4140.04 4137.80 4137.87 4137.83 4133.70 4139.66 4140.27 4140.23 4137.83 4137.41 4132.99 0102  
 7F2 4150.26 4150.14 4147.73 4147.80 4147.77 4145.21 4151.23 4151.84 4151.80 4149.40 4149.01 4142.86 0102  
 5E 4159.24 4159.21 4156.72 4156.85 4156.78 4153.34 4159.30 4159.94 4159.90 4157.48 4157.06 4151.22 0102  
 1A2 4169.79 4169.87 4167.24 4167.42 4167.33 4163.96 4169.91 4170.56 4170.52 4168.07 4167.67 4161.87 0102  
 8F2 4222.16 4218.67 4220.17 4221.15 4220.66 4221.21 4229.10 4229.22 4229.21 4226.77 4226.29 4223.46 1001  
 9F2 4315.07 4309.77 4313.25 4312.56 4312.90 4317.16 4325.55 4325.57 4325.57 4324.57 4323.75 4319.21 0011  
 6E 4318.27 4313.12 4316.42 4315.80 4316.11 4320.05 4328.36 4328.42 4328.42 4327.43 4326.64 4322.15 0011  
 4F1 4318.76 4313.63 4316.91 4316.32 4316.61 4320.77 4329.08 4329.14 4329.14 4328.13 4327.33 4322.58 0011  
 7A1 4319.47 4314.36 4317.58 4316.88 4317.23 4320.94 4329.26 4329.30 4329.30 4328.24 4327.45 4322.72 0011  
 10F2 4355.30 4354.00 4352.93 4352.22 4352.58 4349.55 4355.75 4356.47 4356.42 4355.38 4355.03 4348.77 0201  
 5F1 4369.56 4368.44 4367.15 4366.47 4366.81 4364.06 4370.19 4370.94 4370.90 4369.82 4369.39 4363.31 0201  
 11F2 4384.37 4383.44 4381.90 4381.31 4381.61 4379.39 4385.50 4386.28 4386.23 4385.12 4384.63 4379.10 0201  
 7E 4432.57 4428.16 4430.70 4430.93 4430.82 4431.51 4439.51 4439.78 4439.77 4438.62 4438.12 4446.41 1100  
 6F1 4531.92 4525.69 4530.18 4528.76 4529.47 4533.89 4542.43 4542.60 4542.60 4542.94 4542.06 4543.76 0110  
 12F2 4538.52 4532.39 4536.76 4535.35 4536.05 4540.23 4548.75 4548.93 4548.92 4549.25 4548.46  
 8E 4596.19 4594.10 4593.81 4592.49 4593.15 4591.06 4597.40 4598.30 4598.24 4598.54 4598.14 4592.03 0300  
 2A2 4599.21 4597.32 4596.84 4595.47 4596.16 4593.84 4600.05 4600.99 4600.93 4601.15 4600.68 4595.32 0300  
 8A1 4599.50 4597.61 4597.14 4595.77 4596.45 4594.09 4600.31 4601.24 4601.18 4601.40 4600.94 4595.56 0300  
 9A1 5139.46 5140.26 5136.04 5136.96 5136.50 5129.61 5137.69 5138.23 5138.20 5133.43 5132.95  
 13F2 5162.35 5163.13 5158.90 5159.76 5159.33 5153.51 5161.64 5162.18 5162.14 5157.36 5156.86  
 9E 5190.02 5190.83 5186.59 5187.53 5187.06 5179.54 5187.62 5188.19 5188.15 5183.38 5182.92  
 14F2 5230.83 5231.61 5227.35 5228.26 5227.80 5223.19 5231.29 5231.88 5231.84 5227.07 5226.58  
 10E 5250.74 5251.61 5247.26 5248.24 5247.75 5241.38 5249.44 5250.05 5250.01 5245.21 5244.71

7F1 5251.11 5252.03 5247.62 5248.62 5248.12 5241.95 5249.99 5250.60 5250.56 5245.74 5245.21  
 10A1 5263.12 5264.07 5259.64 5260.69 5260.17 5252.98 5260.99 5261.62 5261.57 5256.74 5256.25  
 15F2 5389.49 5389.12 5386.22 5386.34 5386.28 5380.28 5388.46 5389.13 5389.09 5385.65 5385.18  
 8F1 5407.65 5407.43 5404.32 5404.44 5404.38 5399.21 5407.39 5408.08 5408.03 5404.55 5404.00  
 11E 5443.79 5443.50 5440.43 5440.55 5440.49 5436.67 5444.91 5445.60 5445.55 5442.07 5441.56  
 16F2 5448.46 5448.25 5445.12 5445.32 5445.22 5439.89 5448.04 5448.75 5448.70 5445.18 5444.63  
 9F1 5456.23 5456.08 5452.87 5453.07 5452.97 5448.18 5456.35 5457.07 5457.02 5453.51 5453.00  
 17F2 5461.75 5461.58 5458.40 5458.63 5458.51 5453.95 5462.10 5462.83 5462.78 5459.27 5458.74  
 10F1 5481.28 5481.36 5477.89 5478.20 5478.04 5472.77 5480.85 5481.62 5481.57 5478.00 5477.48  
 11A1 5494.55 5491.14 5491.71 5492.87 5492.29 5490.89 5500.80 5501.04 5501.03 5497.44 5496.82  
 18F2 5522.22 5518.96 5519.32 5520.51 5519.92 5519.56 5529.44 5529.72 5529.70 5526.08 5525.43  
 12E 5535.34 5532.19 5532.45 5533.73 5533.09 5531.55 5541.36 5541.66 5541.65 5538.00 5537.40  
 19F2 5586.40 5581.38 5583.71 5583.30 5583.50 5585.56 5595.86 5596.04 5596.03 5593.84 5592.93 5587.98 0012  
 12A1 5605.55 5600.39 5602.86 5602.35 5602.60 5605.70 5615.91 5616.12 5616.11 5613.96 5613.05  
 11F1 5613.48 5608.52 5610.75 5610.37 5610.56 5613.62 5623.93 5624.13 5624.12 5621.91 5621.00  
 20F2 5613.76 5608.85 5611.00 5610.59 5610.79 5613.74 5624.01 5624.22 5624.21 5621.98 5621.09 5623.00 0012  
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 21F2 5626.56 5621.83 5623.78 5623.46 5623.62 5625.37 5635.54 5635.79 5635.78 5633.52 5632.65 5628.40 0012  
 13A1 5628.17 5626.68 5624.99 5624.41 5624.70 5619.91 5628.39 5629.13 5629.08 5626.93 5626.27  
 14E 5635.89 5634.54 5632.71 5632.12 5632.42 5627.67 5636.03 5636.82 5636.77 5634.60 5634.06  
 22F2 5656.26 5654.97 5653.02 5652.46 5652.74 5648.42 5656.70 5657.53 5657.47 5655.28 5654.59  
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 15E 5670.70 5669.58 5667.46 5666.97 5667.22 5662.41 5670.62 5671.49 5671.43 5669.19 5668.65  
 3A2 5680.53 5679.37 5677.30 5676.77 5677.04 5672.66 5680.88 5681.75 5681.69 5679.49 5678.92  
 23F2 5682.99 5681.89 5679.71 5679.22 5679.46 5676.22 5684.49 5685.36 5685.30 5683.08 5682.57  
 14A1 5696.97 5696.14 5693.67 5693.25 5693.46 5689.50 5697.67 5698.58 5698.52 5696.24 5695.68

16E 5706.53 5705.77 5703.20 5702.83 5703.01 5699.08 5707.23 5708.15 5708.09 5705.80 5705.21  
 24F2 5726.89 5722.61 5724.16 5724.56 5724.36 5723.81 5733.78 5734.19 5734.16 5731.85 5731.24  
 14F1 5744.31 5740.24 5741.52 5742.04 5741.78 5741.63 5751.57 5752.00 5751.98 5749.59 5748.92  
 15A1 5782.67 5774.33 5780.47 5781.15 5780.81 5785.21 5797.26 5797.16 5797.17 5795.30 5794.48 5790.25 2000  
 25F2 5818.86 5811.90 5816.38 5815.20 5815.79 5819.63 5830.40 5830.64 5830.62 5829.83 5828.82 5819.72 0111  
 15F1 5821.64 5815.57 5819.04 5817.88 5818.46 5821.64 5832.11 5832.42 5832.41 5831.54 5830.55  
 17E 5829.35 5823.51 5826.70 5825.54 5826.12 5828.74 5839.13 5839.48 5839.46 5838.57 5837.65  
 16A1 5831.61 5825.58 5829.02 5828.11 5828.56 5831.18 5841.72 5842.03 5842.01 5841.00 5840.07  
 4A2 5839.57 5833.87 5836.89 5835.85 5836.37 5839.67 5850.02 5850.40 5850.38 5849.47 5848.53  
 18E 5839.61 5833.86 5836.92 5835.80 5836.36 5839.56 5849.95 5850.31 5850.29 5849.35 5848.43  
 26F2 5840.79 5834.85 5838.14 5837.03 5837.58 5841.14 5851.57 5851.92 5851.90 5851.00 5850.06 5826.65 0111  
 16F1 5844.02 5838.29 5841.35 5840.29 5840.82 5844.24 5854.62 5854.99 5854.97 5854.04 5853.10  
 27F2 5855.35 5846.56 5853.09 5852.40 5852.75 5859.08 5871.06 5871.04 5871.05 5870.40 5869.38  
 28F2 5881.11 5878.78 5877.99 5876.79 5877.39 5873.93 5882.56 5883.48 5883.42 5882.56 5882.04  
 17F1 5893.98 5891.89 5890.82 5889.60 5890.21 5886.67 5895.02 5896.03 5895.97 5895.07 5894.51  
 29F2 5907.20 5905.26 5904.01 5902.81 5903.41 5900.12 5908.42 5909.46 5909.40 5908.48 5907.85  
 18F1 5920.46 5918.75 5917.19 5916.10 5916.65 5913.77 5922.03 5923.10 5923.03 5922.09 5921.40  
 17A1 5934.13 5925.91 5931.79 5930.71 5931.25 5935.21 5946.15 5946.47 5946.46 5945.91 5945.03  
 19E 5950.84 5945.84 5948.19 5947.96 5948.08 5948.12 5958.17 5958.75 5958.71 5957.64 5956.96  
 18A1 5962.23 5954.66 5959.91 5959.17 5959.54 5964.79 5976.72 5976.74 5976.74 5976.52 5975.43 5968.09 1200  
 30F2 5995.18 5984.56 5993.23 5991.61 5992.42 6001.57 6014.30 6014.09 6014.11 6014.35 6013.05 6004.69 0020  
 20E 6033.25 6022.13 6031.39 6029.55 6030.47 6040.79 6053.81 6053.54 6053.56 6054.01 6052.62 6043.87 0020  
 31F2 6049.12 6042.10 6046.59 6044.78 6045.68 6049.83 6060.57 6061.01 6060.99 6061.44 6060.36 6054.64 0210  
 19F1 6056.02 6049.30 6053.44 6051.60 6052.52 6056.07 6066.62 6067.13 6067.10 6067.52 6066.55  
 32F2 6061.51 6054.75 6058.91 6057.08 6058.00 6061.49 6072.09 6072.59 6072.56 6072.99 6072.09 6065.32 0210  
 19A1 6125.35 6122.45 6122.17 6120.38 6121.28 6118.47 6126.95 6128.14 6128.07 6128.56 6127.87  
 33F2 6428.57 6429.23 6424.35 6425.37 6424.86 6416.73 6427.16 6427.80 6427.75 6421.95 6421.36

20A1 6461.32 6461.93 6457.04 6458.01 6457.53 6451.16 6461.62 6462.25 6462.21 6456.40 6455.78  
34F2 6778.71 6775.22 6775.02 6776.35 6775.68 6773.08 6785.16 6785.51 6785.49 6780.81 6780.09  
35F2 6824.22 6820.90 6820.54 6822.13 6821.34 6819.11 6831.07 6831.50 6831.47 6826.75 6826.02  
5A2 6905.21 6900.28 6901.64 6901.61 6901.63 6903.43 6915.77 6916.13 6916.11 6912.82 6911.76

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<sup>a</sup> CCSD(T) cc-pVTZ. <sup>b</sup> icACPF cc-pVTZ. <sup>c</sup> CCSD(T) cc-pVTZ extrapolated to full CI. <sup>d</sup>  
icACPF cc-pVTZ extrapolated to full CI. <sup>e</sup>  $V^{aberr1}$  plus non-adiabatic corrections. <sup>f</sup> taken  
from Ref. 27.

## FIGURES

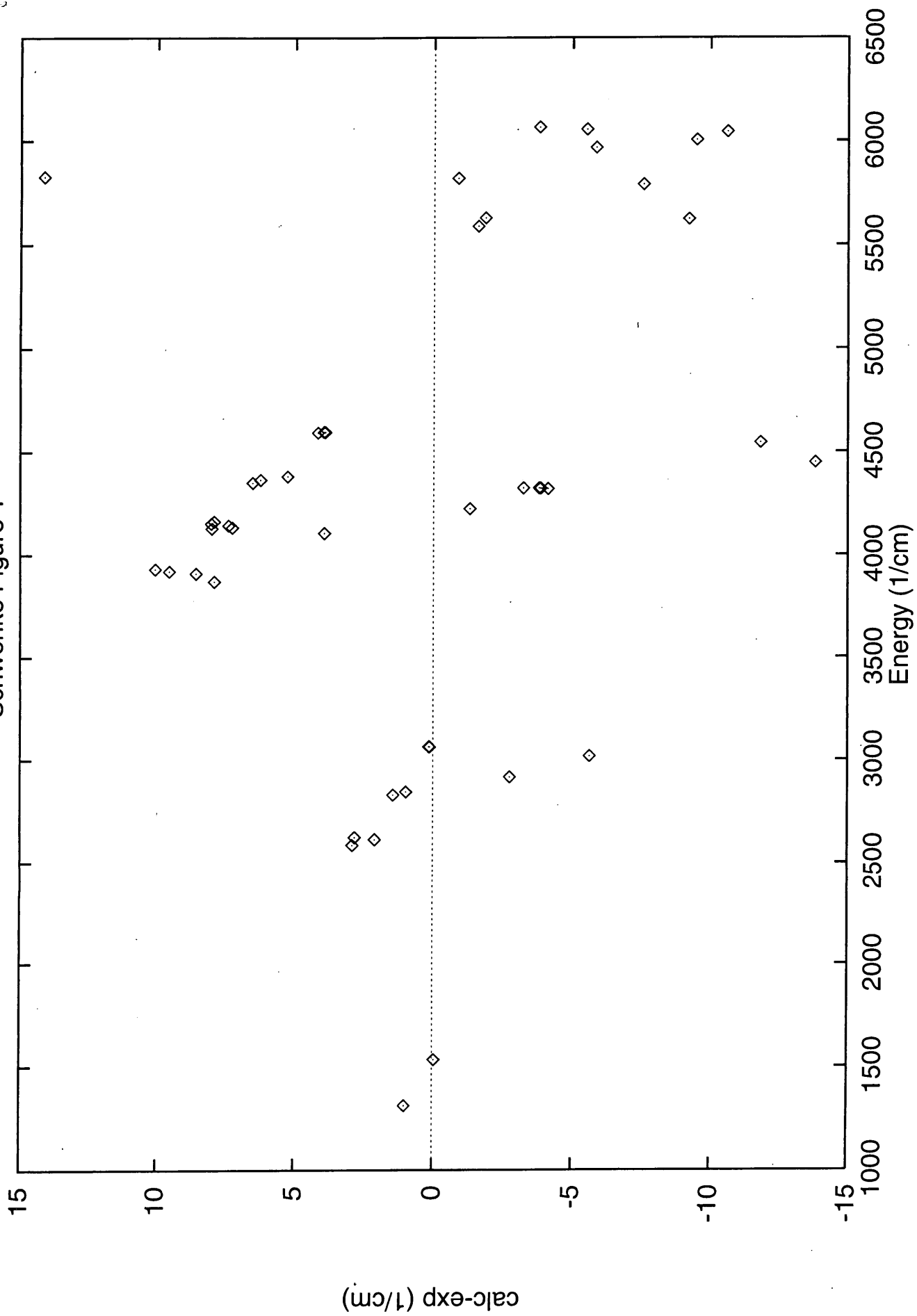
FIG. 1. Vibration energy errors from CCSD(T) cc-pVTZ PES

FIG. 2. Vibration energy errors from PES  $V^{ab}$

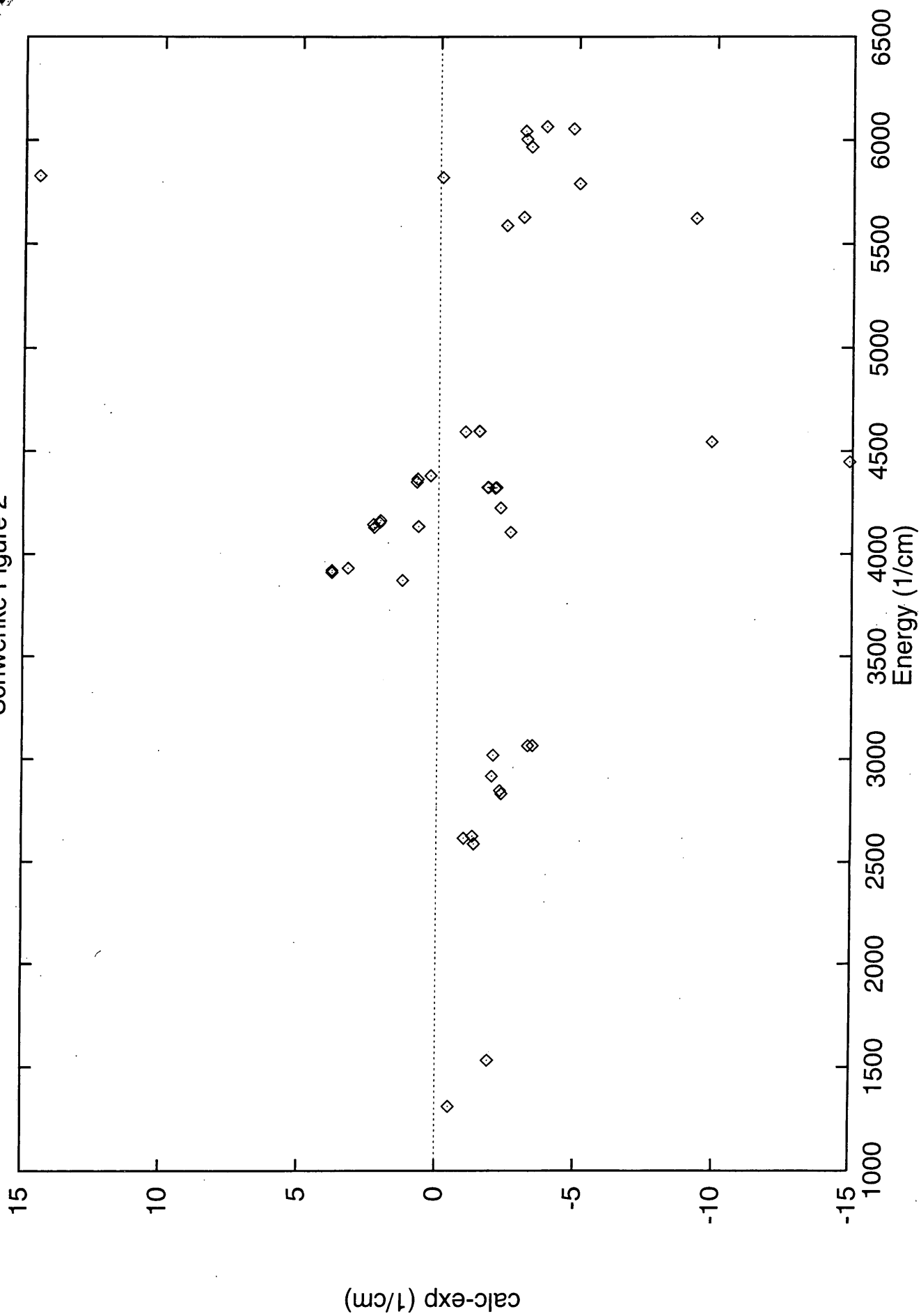
FIG. 3. Vibration energy errors from PES  $V^{abc}$

FIG. 4. Vibration energy errors from PES  $V^{aberr1}$  plus non-adiabatic correction

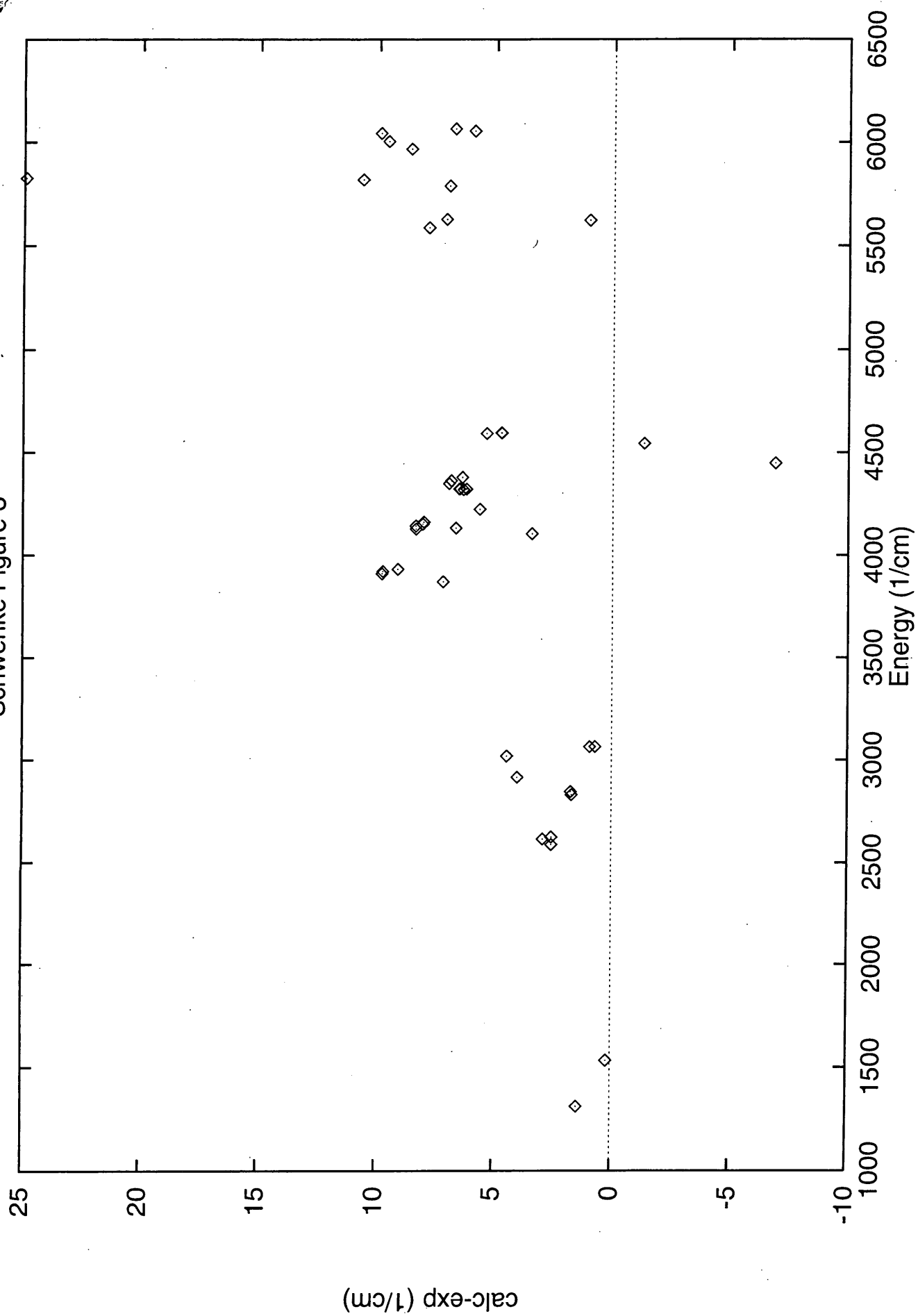
Schwenke Figure 1



Schwenke Figure 2



Schwenke Figure 3





Schwenke Figure 4

